

¹³C NMR Structural Determination of the Coals in the Premium Coal Sample Bank

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Introduction

Solid state ¹³C cross polarization (CP) magic angle spinning (MAS) NMR experiments have become very useful for the study of the structure of coal and other fossil fuels (1, 2). Solid state NMR techniques have the advantage over liquid NMR methods because the whole solid coal can be analyzed in a nondestructive manner and no assumption need be made that the soluble portion represents the whole organic portion of the coal. From CP/MAS experiments twelve NMR structural parameters may be determined including the aromaticity, f_a , that give information on the carbon skeletal backbone. The variation of the NMR structural parameters for coals of different rank from lignite to anthracite has been demonstrated (3). The coals in the Premium Coal Sample Bank (PCSB) have been included in the set of coals studied at the Advanced Combustion Engineering Research Center. The NMR data obtained on these coals will be used to provide chemical structural parameters for refinement of the devolatilization sub-model of the PCGC-2 combustion model.

This paper reports the twelve structural parameters for two of the PCSB coals, Pittsburgh #8 (HVB) and Blind Canyon (HVB). These data were derived from integrated intensities in a normal CP/MAS experiment along with a complete set of dipolar dephasing experiments. In addition, the proton spin lattice relaxation times for these coals have been determined. From relaxation experiments on the Pittsburgh #8 coal there is some evidence of heterogeneity between different sample vials of the same standard coal.

Experimental

The coal samples studied were Argonne Premium Coal Bank samples of: Pittsburgh #8, high volatile bituminous, COAL_ID: 401, vials 137,140,157,159 and Blind Canyon Seam, high volatile bituminous, COAL_ID: 601, vial 90. All spectra were taken on a Bruker CXP-100. A single contact of 2.5 ms was employed for all T_1 and dipolar dephasing experiments together with a pulse delay time of 1.0 ms which is greater than $5T_1$'s for both coals. The samples were opened in a nitrogen glove bag, placed in a capped boron nitride rotor, and spun under nitrogen gas except for vials 137 and 159 of the Pittsburgh #8 which were opened in air and then placed immediately in the rotor. All

chemical shielding values are given in ppm with respect to external TMS. The pulse sequence used to measure the proton T_1 indirectly by observing the carbon resonance is described in detail by Axelson (1) and the dipolar dephasing sequence which includes refocusing pulses in both carbon and proton channels has been described by Alemany et. al. (4).

Results and Discussion

Proton Spin Lattice Relaxation

The proton T_1 's are given in Table I for both the aromatic and aliphatic regions of one Blind Canyon vial and for four different vials of the same Pittsburgh #8 coal.

Table I: T_1^H (ms) Values for Two Argonne Coals.

Coal and Vial #	Aliphatic	Aromatic
Pittsburgh #8		
137	192 ± 7	193 ± 6
140	206 ± 9	194 ± 5
157	152 ± 5	140 ± 2
159	151 ± 10	138 ± 5
Blind Canyon		
90	60 ± 3	43 ± 2

\pm = one marginal standard deviation from three parameter fit.

The four different vials of Pittsburgh #8 have T_1^H values that fall into two groups, two with T_1 's of approximately 195 ms and two with values in the 140-150 ms range. To check the reproducibility of the T_1 data, two different experiments were performed on a sample without removing it from the spectrometer. The measured T_1 's were well within one marginal standard deviation (MSD) of each other, implying that the difference in the Pittsburgh #8 is greater than the experimental error. It is postulated that during the physical mixing and grinding of this coal, paramagnetic centers may not have been randomly distributed. The T_1 's measured for both aliphatic and aromatic regions give the same value within two MSD for the Pittsburgh #8 samples demonstrating that spin diffusion is an efficient relaxation mechanism in this sample. For the Blind Canyon sample T_1^H is much shorter than Pittsburgh #8. The T_1 's for the aliphatic and aromatic regions of the spectrum differ by more than three MSD indicating that spin diffusion does not occur throughout the whole sample.

Dipolar Dephasing and Structural Parameters

Under the conditions of the dipolar dephasing experiment the carbon magnetization can be characterized by a decay constant, T_2 , which depends on the strength of the ^1H - ^{13}C dipolar coupling. Characteristic values of T_2 for CH , CH_2 , and CH_3 groups in model compounds and coals have been reported (3, 4, 5, 6). The T_2 decay curve is usually characterized by two time constants: a Gaussian component characterized with a time constant, T_G , for rapidly decaying components (CH and CH_2 groups) and a Lorentzian component with a time constant, T_L , for slowly decaying components (rapidly rotating methyl groups and nonprotonated carbons). An example of the decay curve for the magnetization, $M(t)$, for the aromatic region of Pittsburgh #8 is shown in Figure 1 and was fit to the following equation:

$$M(t) = M_{0L}e^{-t/T_L} + M_{0G}e^{-0.5(t/T_G)^2} \quad 1)$$

where M_{0L} and M_{0G} are the relative amounts of slow and fast decaying carbon magnetization at $t = 0$.

The above equation is applied separately to the decay of the aromatic and aliphatic regions of the spectrum and four parameters (M_{0L} , T_L , M_{0G} , T_G) are determined for each region and are used with integrated intensities, I , over various regions of the spectrum to determine the 12 structural parameters as follows:

$$\begin{aligned} f_a &= (I_{>90} + 2I_{ss})/I_{\text{total}} \\ f_a^C &= I_{>165}/I_{\text{total}} \\ f_{a'} &= f_a - f_a^C \\ f_a^H &= (M_{GO}^{\text{ar}}/M_{\text{total}}^{\text{ar}}) \times f_{a'} \\ f_a^N &= f_{a'} - f_a^H \\ f_a^P &= I_{150-165}/I_{\text{total}} \\ f_a^S &= I_{135-150}/I_{\text{total}} \\ f_a^B &= f_a^N - f_a^S \\ f_{al} &= 1 - f_a \\ f_{al}^H &= (M_{GO}^{\text{al}}/M_{\text{total}}^{\text{al}}) \times f_{al} \\ f_{al}^* &= f_{al} - f_{al}^H \\ f_{al}^O &= I_{50-90}/I_{\text{total}} \end{aligned} \quad 2)$$

where I_{total} is the total integrated intensity of the whole spectrum, I_{ss} is the integrated intensity of the down field spinning sideband and I_{ppm} 's are the integrated intensities over

selected chemical shift ranges in ppm. These structural parameters are listed in Table II for the two coals and the normal CP/MAS spectrum is shown in Figure 2 for Pittsburgh #8 (bottom) and Blind Canyon (top).

Although both of these coals are of the same rank and nearly identical carbon content there are variations in some of the structural parameters. The f_a value for the Pittsburgh #8 is 0.75 while a lower value of 0.64 is found for the Blind Canyon coal indicating that more of the carbon is sp^2 -hybridized in the Pittsburgh #8. From the elemental analysis data (7) the atomic H/C ratio is 0.79 for the Pittsburgh #8 and 0.91 for the Blind Canyon samples. The higher H/C ratio for the Blind Canyon coal is not surprising since this coal contains approximately 15% liptinite which is highly aliphatic and thus hydrogen rich. Using H/C data together with the f_{al}^H and f_a^H values for the two coals one notes that the H/C ratios for the aromatic and aliphatic regions are 0.37 and 2.0 for Pittsburgh #8 and 0.34 and 1.97 for Blind Canyon. This would seem to indicate that both the aliphatic and aromatic regions are quite similar but, as can be seen from the spectra, the aliphatic regions of the two coals appear to be significantly different. If it is assumed that the parameter f_{al}^* represents only methyl groups and the H/C ratio of the aliphatic region appropriately corrected, then the H/C ratio of the remaining aliphatic region for the two coals is 1.3 for Pittsburgh #8 and 1.7 for Blind Canyon. These differences can now be used to rationalize the marked spectral differences observed in the aliphatic regions of the two coals. The aliphatic structure of the Pittsburgh #8 is probably more highly branched, having more CH groups and a lower H/C ratio than the Blind Canyon coal which probably has more straight chains with CH_2 groups or nonsubstituted tetralin-type structures contributing to the higher aliphatic H/C ratio.

This work demonstrates that solid state NMR techniques can be used to distinguish structural differences in coals that are of the same rank as well as determining structural differences in coals of varying ranks. Similar data will be taken on all of the PCSB coals. This data will be used to assess those structural features that make major contributions to devolatilization behavior of the coals in the combustion processes.

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Table II: Structural Distribution of Argonne Coals.

COAL	f_a	$f_{a'}$	f_a^C	f_a^H	f_a^N	f_a^P	f_a^S	f_a^B	f_{al}	f_{al}^H	f_{al}^*	f_{al}^O
PITTSBURGH #8 (HVB)	.75	.75	.00	.28	.47	.06	.17	.30	.25	.14	.11	.03
BLIND CANYON (HVB)	.65	.64	.01	.22	.42	.07	.15	.27	.35	.27	.08	.04

f_a = Fraction of total carbon that is sp^2 -hybridized.

$f_{a'}$ = Fraction of total carbon that is sp^2 -hybridized and in an aromatic ring.

f_a^C = Fraction of total carbon that is carbonyl - $\delta > 165$ ppm.

f_a^H = Fraction of total carbon that is sp^2 -hybridized and protonated.

f_a^N = Fraction of total carbon that is sp^2 -hybridized and nonprotonated.

f_a^P = Fraction of total carbon that is phenolic or phenolic ether - $\delta = 150 - 165$ ppm.

f_a^S = Fraction of total carbon that is sp^2 -hybridized and alkylated - $\delta = 135 - 150$ ppm.

f_a^B = Fraction of total carbon that is sp^2 -hybridized and at a bridgehead position.

f_{al} = Fraction of total carbon that is sp^3 -hybridized.

f_{al}^H = Fraction of total carbon that is sp^3 -hybridized and CH or CH_2 .

f_{al}^* = Fraction of total carbon that is sp^3 -hybridized and CH_3 or nonprotonated.

f_{al}^O = Fraction of total carbon that is sp^3 -hybridized and bonded to oxygen - $\delta = 50-90$ ppm.

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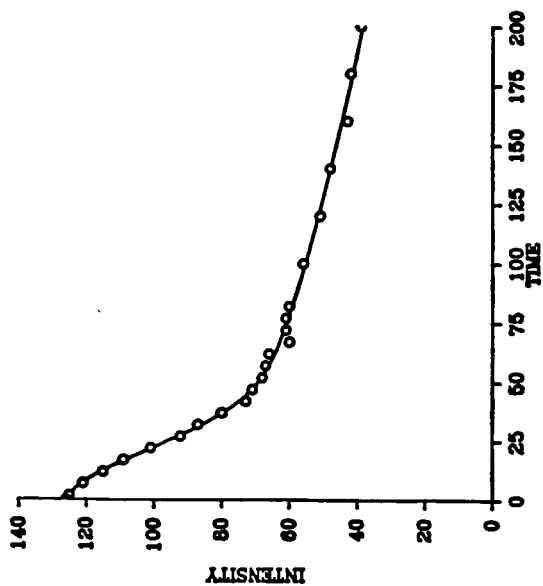


Figure 1. Dipolar dephasing decay curve for the aromatic carbons of Pittsburgh #8. Times are in μ s.

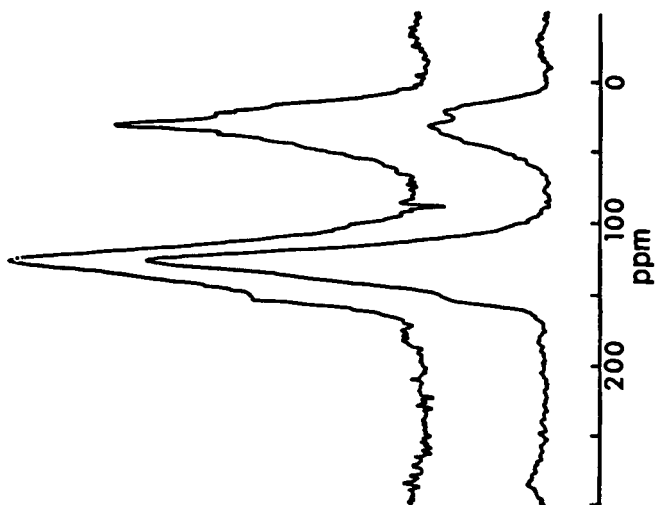


Figure 2. CP/MAS spectra of Blind Canyon (top) and Pittsburgh #8 (bottom).